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(19)

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(54) IMPROVED POLYOLEFIN COMPOSITIONS

(71) We, MONSANTO CHEMICALS LIMITED, a British Company, of Monsanto House, 10—18 Victoria Street, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyolefin compositions and particularly to improved antistatic polyolefin compositions.

It is well known that in use polyolefin resins such as polyethylene normally acquire, by for example frictional contact with other materials, an electrostatic charge which results in a substantial accumulation, over a period of time, of a surface layer of dust. To combat this it has been proposed to incorporate in the material an antistatic agent, but this proposal has not always proved effective. Sometimes good results may be obtained, whilst in other cases severe dust accumulation occurs. The degree of dust pick-up is usually not even uniform over the surface of the same article, exhibiting "trees", "ridges", lines and other patterns.

We have now found that a certain combination of additives gives an improved antistatic effect when incorporated in a polyolefin, and in fact the results are better than when either additive is used separately.

The invention comprises an antistatic polyolefin resin composition comprising as antistatic additives an amine having the formula

$$R-N-\left[(CH_2-CHR'-O)_mH\right]_nH_{2-n}$$

wherein R is a C_6—C_{18} aliphatic hydrocarbyl group, R′ is hydrogen or methyl, m is an integer from 1 to 8 inclusive and n is 1 or 2, and an amide of the formula

$$X-CO-N-\left[(CH_2-CHX'-O)_pH\right]_qH_{2-q}$$

wherein X— is a C_6—C_{18} aliphatic hydrocarbyl group, X′ is hydrogen or methyl, p is an integer from 1 to 8 inclusive and q is 1 or 2.

Preferably in the above formulae m and p are each 1, and n and q are each 2. Preferably R′ and X′ are each hydrogen. The preferred amines and amides are those in which R and X— are C_{10}—C_{14} aliphatic hydrocarbyl groups and particularly N,N-dihydroxyethyllaurylamine and N,N-dihydroxyethyl lauramide.

The additives are preferably present in a relative proportion by weight of from 10:90 to 90:10, more preferably from 25:75 to 75:25. A mixture comprising approximately 50 weight percent each of the amine and the amide, such as for example equal weights of N,N-dihydroxyethyl laurylamine and N,N-dihydroxyethyl lauramide, usually gives very satisfactory results in practice.

The total amount of the antistatic agent added will depend largely on the degree of antistatic protection required but in practice percentages of from 0.01 to 1.0 by weight of the composition represent the full range of potential commercial interest. Within this range weight percentages of from 0.05 to 0.4 and especially 0.1 to 0.2 are particularly preferred. Larger amounts can be present in concentrated "master-batch" compositions intended to be diluted with additional quantities of resin before use.

The polyolefin can be any resinous polymer

or copolymer of an olefin monomer but in general the major interest in this field lies in homopolymers such as polyethylene and polypropylene, and copolymers such as those of an olefin with an unsaturated ester, for example vinyl acetate. Polyethylene is very often the preferred resin in the composition of the invention and can be high or low density material.

The composition can of course contain other additives such as for example pigments, antioxidants or slip additives.

The components of the composition can be mixed by any convenient method, for example by tumbling the additives with pellets or particles of the resin optionally followed by extrusion into a strand that can be chopped up to form pellets. Preferably, however, the components are blended at a temperature sufficiently high to plastify the resin for example in an internal or roll mixer.

The composition of the invention can be fabricated by any of the methods normally used for polyolefin resins, including extrusion, injection-moulding, blow-moulding or casting. It can for example be extruded and blown into film, or used for extrusion-coating, blow-moulded into bottles, toys or other hollow articles, injection moulded into a variety of shapes, or cast into film or (by rotational casting) into large containers. The composition is in fact particularly useful for use in a process of extrusion-coating a substrate as described below.

In an extrusion coating process, a substrate surface is brought into contact with an extruded molten layer of resin and the layer is then allowed to solidify to form an adherent coating on the substrate surface. The linear speed at which the resin composition is extruded is normally very much less than that of the substrate so that the composition becomes drawn, and it is commercially advantageous to operate at as great a rate as possible. However, as the substrate speed is increased, for a fixed rate of extrusion, a terminal speed is reached beyond which rupture of the coating occurs and this terminal speed is known as the "drawdown" for the particular resin employed. Also during extrusion, the width of the deposited layer of resin tends to decrease and the extent of the decrease at a defined extrusion rate is known as the "neck-in". It is clearly desirable to maximise the drawdown/neck-in ratio in normal commercial operations so as to achieve the greatest possible production of coated substrate.

It has now been found that the antistatic additives of the invention are particularly suitable for inclusion in extrusion-coating grades of polyolefin resins since they substantially improve the drawdown/neck-in ratio. At the same time there is usually observed an improvement in the ease with which the resin is released from the chill roll that is usually used in an extrusion-coating process.

The invention accordingly comprises a process of extrusion-coating a substrate with a polyolefin resin composition of the invention.

In the extrusion coating process of the invention, the substrate surface is brought into contact with an extruded molten layer of the resin composition, and this layer is then allowed to solidify to form an adherent coating on the substrate surface. A wide range of substrate surfaces can be extrusion coated. Generally the substrate surface is substantially flat, and it is very often preferred if the substrate is in the form of a sheet or film. Examples of substrate surfaces that are suitable include paper, polypropylene film, "Saran"-coated polypropylene film ("Saran" is the trade mark for a copolymer of vinylidene chloride and vinyl chloride), aluminium foil, cellulose acetate film and polyethylene terephthalate film. Paper is usually the preferred substrate.

The extrusion coating operation can take place according to normal practice. Thus it is convenient to extrude a molten layer of the resin composition vertically downwards through a slit die spaced a few inches above the nip between a pair of rollers into which the substrate is fed, the roller contacting the molten layer preferably being chilled so as to solidify the layer. This roller can have a matt or satin finish so that a similar finish is imparted to the coating, or it can be embossed so that a corresponding pattern is produced. The chilled roller can if desired be polished so as to impart a high gloss surface to the coating.

Treatment of the substrate by an electric discharge or a chemical primer has been found to assist adhesion of the molten layer.

The temperature of the molten layer is naturally above the melting point of the resin but should not be so high that an undesirable degree of decomposition or oxidation can take place during the time that the resin is maintained at this temperature in the extruder and in the "air gap" between the extrusion die and the chilled roller. A limited degree of decomposition or oxidation assists adhesion and is therefore to be desired, but odour formation can take place where the melt temperature is too high. The temperature chosen also depends to some extent on the intended use of the coated substrate, for a relatively high temperature can induce molecular cross linking, which may or may not be desirable. For example, a cross-linked coating has good strength, but it is on the other hand difficult to heat-seal a coating that has a large number of cross-links so that a relatively low melt temperature would be chosen where a heat-sealable coating is desired. In general the temperature is normally between 260 and 330° C., and very often between 280 and 310° C.

The "air gap" between the extrusion die and the chilled roller is normally at least 1

inch and not normally greater than 10 inches, from 3 to 6 inches, for example about 4 to 5 inches, often being very suitable.

The linear speed at which the resin composition is extruded is normally very much less than that of the substrate, and can for example be up to about 20 feet per minute, very often from 0.5 to 5 feet per minute, such as about 1 foot per minute. The effect of this difference in speed is that the composition becomes drawn, and the final coating is thus considerably thinner than the molten layer issuing from the die. A reduction in lateral width also takes place and allowance for this needs to be made when choosing the dimensions of the die.

The thickness of the finished coating can for example be up to about 0.005 inch, but generally a thinner coating, for instance 0.00015 to 0.002 inch is preferred. Very often a thickness from 0.0005 to 0.001 inch is particularly suitable.

The coated substrate leaving the chilled roller can be wound up and stored until required for use. It can for example be used for wrapping and other packaging purposes, for instance of food.

The coating can if desired be treated with an electric discharge to improve adhesion of any printing ink that may subsequently be applied to it. It has previously been suggested that such a discharge also improves antistatic properties but it is a feature of the present invention that good antistatic properties are obtainable without such discharge treatment.

The invention is further described in the following Examples.

EXAMPLE 1.

This Example describes a polyethylene composition according to the invention and its use in extrusion coating process according to the invention, and demonstrates the advantages obtained.

Polyethylene resin of melt index 6.4 grams per ten minutes and density 0.916 grams per cubic centimetre was blinded on a bridge Banbury mill with 0.1 percent by weight of N,N-dihydroxyethyl lauramide and 0.1 percent by weight of N,N-dihydroxyethyllaurylamine.

The resulting composition and a "blank" of the polyethylene resin alone were each extruded separately through a 2½ inch Peco extruder fitted with a slit coating die deckled to 22½ inches, coated on to paper and then treated with a corona discharge. The drawdown/neck-in ratio and anti-static properties of each coating were determined.

The anti-static properties of each coating were assessed by taking a 12.5 by 7.5 centimetre sample of the coated paper, electrically charging it by contact with a charged plate of chromium plated steel, and measuring the percentage of the charge on the surface that leaked away upon application of an earthed probe. This measurement was made using an electrometer and the result was quoted as the percentage charge increase (PCI) which is defined as

$$\frac{\text{charge collected from sample in 30 seconds} \times 100}{\text{charge on chrome plate in 30 seconds}}$$

It has been found that samples having a PCI greater than 20 per cent have good anti-static properties.

The results of the tests are shown in the following Table:

Composition	Neck-in at 100 feet per minute	Drawdown in feet per minute	PCI%
"Blank"	1.4 inch	440	2
Composition of invention	1.4 inch	510	50

It can be seen that the composition of the invention has excellent anti-static properties yet has a better drawdown/neck-in ratio than the "blank".

Good antistatic properties were also obtained from the composition of the invention when the corona discharge treatment was omitted.

EXAMPLE 2.

This Example describes another polyethylene composition according to the invention and its use in an extrusion coating process according to the invention, and shows that a considerable improvement in antistatic properties is obtained. Comparative examples are given to show that the combination of additives gives better results than when either additive is used separately.

The additives shown in the table below were blended with the polyethylene used in Example 1 by the same method, and the resulting compositions were extrusion-coated on to paper as before. The Table also gives the percentage charge increase (PCI) measured for each blend.

% w/w N,N-dihydroxyethyl lauramide	% w/w N,N-dihydroxyethyl laurylamine	PCI%
0.05	0.05	50
0.1	Nil	26
Nil	0.1	3
Nil	Nil	2

These results demonstrate the excellent antistatic properties of the composition of the invention compared with those of composition containing only one of the additives.

WHAT WE CLAIM IS:—

1. An antistatic polyolefin resin composition comprising as antistatic additives an amine having the formula

$$R-N-\left[(CH_2-CHR'-O)_mH\right]_n H_{2-n}$$

wherein R is a $C_{[illegible]}$—C_{18} aliphatic hydrocarbyl group, R′ is hydrogen or methyl, m is an integer from 1 to 8 inclusive and n is 1 or 2, and an amide of the formula

$$X-CO-N-\left[(CH_2-CHX'-O)_pH\right]_q H_{2-q}$$

wherein X— is a $C_{[illegible]}$—C_{18} aliphatic hydrocarbyl group, X′ is hydrogen or methyl, p is an integer from 1 to 8 inclusive and q is 1 or 2.

2. A composition according to Claim 1, in which m and p are each 1.

3. A composition according to either of Claims 1 and 2, in which n and q are each 2.

4. A composition according to any of the preceding claims, in which R and X are C_{10}—C_{14} aliphatic hydrocarbyl groups.

5. A composition according to Claim 1, in which the amine is N,N-dihydroxyethyl-laurylamine and the amide is N,N-dihydroxyethyl lauramide.

6. A composition according to any of the preceding claims, in which the additives are present in a relative proportion by weight of from 25:75 to 75:25.

7. A composition according to any of the preceding claims, in which the total amount of antistatic agent is from 0.05 to 0.4 percent by weight of the composition.

8. A composition according to any of the preceding claims, in which the polyolefin is polyethylene.

9. A composition according to Claim 1, substantially as described in Example 1.

10. A composition according to Claim 1, substantially as described in Example 2.

11. A process of extrusion-coating a substrate with a polyolefin resin composition according to Claim 1.

12. A process according to Claim 11, in which there is used a resin composition according to any of Claims 2 to 9.

13. A process according to either of Claims 11 and 12, in which the substrate comprises paper.

14. A process according to any of Claims 11 to 13, in which the coating is treated with an electric discharge.

15. A process according to Claim 11 substantially as described in Example 1.

16. A process according to Claim 11 substantially as described in Example 2.

17. A coated substrate that has been produced by a process according to any of Claims 11 to 15.

18. A coated substrate that has been produced by a process according to Claim 16.

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